Band structure of Covalent Solids

DISSERTATION

submitted in partial fulfillment of the requirements for the Degree of M.Sc.
(Physical chemistry)

BY

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work carried out under supervision of
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TO

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STATEMENT

I hereby inform that the matter presented in this dissertation entitled "**Band structure of covalent solids**" is based on the result of investigation carried out by me at School of Chemical Sciences, Goa University under the supervision of Dr.Vivekanand V.Gobre and the same has not been submitted for the award of Msc degree.

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CERTIFICATE

This is to certify that dissertation entitled "Band structure of covalent solids" is a bonafide work carried out by Miss Gouraja Gurudas Gad under my supervision in partial fulfillment of requirements for the award of of the degree of M.Sc in chemistry at the School of Chemical Sciences, Goa University.

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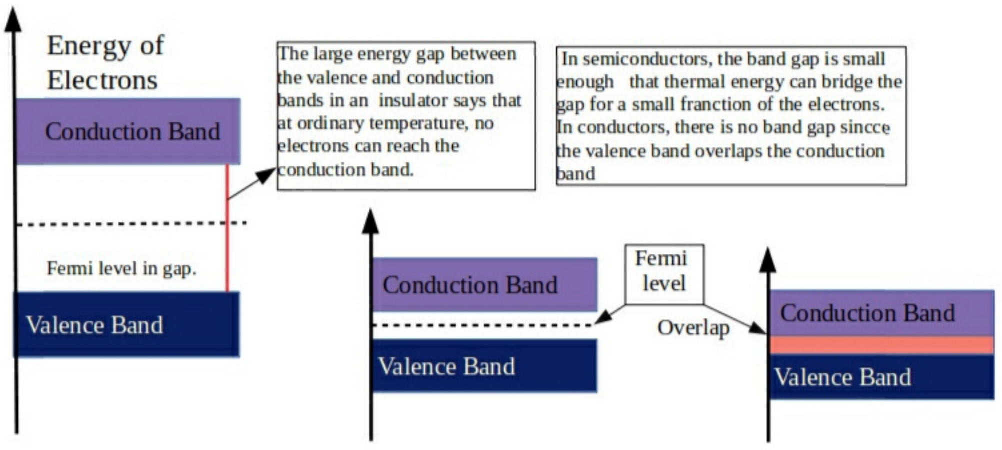
Introduction

Semiconductor are material whose electron properties are intermediate between those of metal and insulators. These characteristics are determined by the structure of the crystal, bonding characteristic, electronic energy bands, and also by the fact that unlike metals, a semiconductor has both the positive(hole) and the negative (electron) carriers of electricity whose density can be controlled by doping the pure semiconductor with chemical impurities during the crystal growth. To classify the solid by their electrical properties, it should be understood that there are three types of materials, metal, semiconductor and insulator.



The large energy gap between the valence and conduction bands in an insulator says that at ordinary temperature, no electrons can reach the conduction band.

In semiconductors, the band gap is small enough that thermal energy can bridge the gap for a small franction of the electrons. In conductors, there is no band gap sincce the valence band overlaps the conduction band

a. Insulator b. Semiconductor c. Conductor

Figure 1.1: Shows the Band Gap in Semiconductors, Insulators and in Metals.

The group III-V Semiconductor such as Gallium arsenide (GaAs), Silicon Carbide (SiC) , Silicon(Si), Indium arsenide(InAs), Boron arsenide (BAs), Aluminium arsenide(AlAs), Gallium nitride (GaN) are very important material in fabrication of microwaves, optoelectronic and electronic devices [**?**]. These semiconductors has good basis for technological application such as light emitting diodes, lasers, integrated circuits, filters, modulators and photo detectors.

Aluminium arsenide having Zinc blend structure which is a binary semiconductor with an indirect gap[**?**]. It has wide range application in optoelectronic, telecommunications, laptops, solar cells, compact disc, therefore study of these semiconductors is intensively attracted by the researcher[**?**][**?**]. In fabricating heterostructure and tuneable devices in the visible wavelength region and optoelectronic devices, InAs and AlAs has great significance.

Indium Arsenide(InAs) semiconductor is a direct band Semiconductor and shows application in high power and high temp electronics also used in diode laser, in constructing infrared detectors for wavelength range of and formation 1-3.8μm of quantum dots in monolayer[**?**].

wide gap semiconductors such as Gallium nitride (GaN), Aluminium nitride (AlN) and Boron nitride (BN) are actively investigated in view of their promising potential for short wavelength electroluminiscence devices and high temperature, high power, high frequency electronics. These semiconductors are mostly used in micro and optoelectronics therefore they recieved considerably attention from both theoretically and experimentally[**?**].

Cadmium selenide (CdSe), Cadmium sulphidde(CdS), Cadmium telluride (CdTe) are also important material in optoelectronic devices. These have been several experimental and theoretical studies in this material. Ab initio calculations based on norm conserving pseudopotential and density functional using using local density approximation have been perform to determine its elastic, electronic, and dynamical properties[**?**]. Diamond has high hardness and bulk modulus and it is widely used in the mold abrasive and machinery industry. it is the most important part of optical performance due to its excellent optical performance. Silicon (Si) is main semiconducting material and Germanium (Ge) semiconductor has high carrier mobility. It is also used in infrared optical properties, the solar cells, the transistor, thermoelectric material, radiation detector etc

The aim of this work is to prospect the electronic energy band from the band structure of Zinc blende type such as Zinc sulphide (ZnS), Zinc selenide (ZnSe), Zinc telluride (ZnTe), Cadmium selenide (CdSe), Cadmium sulphidde (CdS), Cadmium telluride (CdTe), Gallium arsenide (GaAs), Gallium antimonide (GaSb), Gallium phospide (GaP), Gallium nitride (GaN), Silicon Carbide (SiC) , Indium arsenide(InAs), Indium phosphide (InP), Silicon(Si), Boron arsenide (BAs), Aluminium arsenide (AlAs), Aluminium phosphide (AlP), Aluminium arsenide (AlAs), Boron Nitride (BN), Boron phosphide (BP), diamond (C), Tin (Sn), Germanium (Ge), Silicon (Si). These covalent solids are studied using NWchem plane wave (NWPW) module which uses pseudopotential and plane wave basis set to perform density functional theory calculation. NWPW is a module which basically used to perform band task where in a band structure code is used for calculating crystal and surface with small band gaps e.g semiconductors and metals. In this study we use pbe96 and Bhlyp functional of local density approximation for determining band structure of solids.

2

Theoretical methods

Computational chemistry is also called as molecular modelling and it is the study of chemical problems using computer as a tool. Computational chemistry deals with

1. Molecular geometry: In molecular geometry it studies the shape of the molecule i.e. band length, bond angles and dihedral.

2. Chemical reactivity: In this we determine nucleuophillic site or the electrophillic site in the particular reaction.

3. IR, UV and NMR spectra.

4. The interaction of a substrate with an enzyme. This study used in drug designing.

5.The physical properties of the substance It determine the different properties of the molecule like its melting point, strength, fores of interaction etc.

The tools of computational chemistry are:

Molecular mechanics(MM) which is based on the no. of atoms held together by a bond by knowing the bond length and the angle between them, the energy it takes to bend and stretch the given atom can be calculated thereby he energy of no. of atoms and bond of a given molecule can be easily studied. Upon geometry optimization we determine its lowest energy and which calculates the geometry of the molecule. This study is useful for the larger molecule for e.g steroid.

Ab initio calculates are based on the Schrödinger equation which depend the electron behavior in the molecule. In this method the solution of the Schrödinger equation for the molecule gives molecule's energy and wavefunction. The wavefunction is being mathematical function that can be used to calculate the electron distribution. Electron distribution determines polarity of the molecule, which part of it likely to be attacked by the nucleophiles or electrophiles. Since Schrödinger equation cannot solve for the molecule with more than one electron. Since considering this approximation, the lesser the serious these are, the better is the Ab initio calculations. Ab initio calculations are reasonably slow; smaller the molecules faster will the completion but it takes relatively more time for the larger molecule.

Semiempirical Calculation(SE) are similar to Ab initio calculations that also depends on Schrödinger equation. In this method very complicated integral are not evaluated instead the program draws on a kind of library integrals that was compile by finding the best fit of calculated entity. Thus introducing of experimental valves into a mathematical procedure to get the best calculated Value is called parameterization. Theory based on the mixing of experiment and theory that makes the method semiemperical. Semiemperical calculations are slower that Molecular mechnics(MM) but faster than Ab initio method.

Density functionals calculations, Similar to Ab initio calculations and Semiemperical calculations that depends on the Schrodinger equation. DFT does not calculate a wavefunction but rather it derives electron density. A functional is a mathematical property related to function. This method are faster than Ab inition but slower than semiemperical Calculations[**?**].

1 Molecular mechanics(MM)

Molecular mechanics is based on mathematical model of a molecule as a collection of the atoms held together by bonds. within the frame work of this model, the energy of the molecule changes with geometry because the bond resist being stretched or bent away from some natural length or angle and the atoms resist being pushed too closely together. Molecular molecules model clearly ignores electron. The principle behind MM is to express the energy of molecule as a funtion of its resistance towards bond stretching, bond bending and atom crowding,and to use this energy equation to find the bond length, angles and dihedral corresponding to the minimum energy Geometry or more precisely to the various possible potential energy surface minima. Developing a forcefield The potential energy of a molecule can be written.

$$E = \sum_{\text{bends}} E_{\text{strech}} + \sum_{\text{angles}} E_{\text{bend}} + \sum_{\text{dihedral}} E_{\text{torsion}} + \sum_{\text{pairs}} E_{\text{nonbond}} \quad (2.1.1)$$

Where,

E_{strech} are energy contribution from bond stretchinglewars2003computational.

E_{bend} are energy contribution from angel bending.

E_{torsion} are energy contribution from torsional motion around single bond torsion.

E_{nonbonds} are energy contribution from interaction between atoms or group which are non bonded.

The sums are over all the bonds, all the angles defined by three atoms. A-B-C, all the dihedral angles. angles defined by four atoms A-B-C-D and all pairs of significants non bonded interactions. The mathematical form of these terms and the parameters in them constitute term. The increase in the energy of a spring when it is stretched. Examples of molecules mechanics. If we consider the application of Molecular Mechanics from the view point of the goals of those who use it, then the main application have been,

1. To calculate the Geometries (and perhaps energies) of small to medium sized (i.e. no polymeric) molecules, very often in order to a reasonable starting Geometry for another type (eg ab initio) of calculation.

2. To calculate the Geometries and energies of polymers(mainly proteins and nucleic acid)

3. To calculate the geometries and energies of transition stats as an aid to organic Synthesis.

4. To generate the potential energy function under which molecules molecules move far molecular dynamics calculation.

$$Vr^N = \sum_{\text{bonds}} k_b(l-l_o)^2 + \sum_{\text{angle}} k_a(\theta-\theta_o)^2 + \sum_{\text{torsion}} \sum_{n} \frac{1}{2} V_n \Big[1 + (\mathrm{n}\omega - \gamma)\Big] + \\ + \sum_{j=1}^{N-1} \sum_{i=j+1}^{N} f_{ij} \left\{ \epsilon_{ij} \left[\left(\frac{r_{oij}}{r_{ij}} \right)^{12} - 2 \left(\frac{r_{oij}}{r_{ij}} \right)^{6} \right] \right\} + \frac{q_i q_j}{4\pi\epsilon_o r_{ij}} \qquad (2.1.2)$$

Equation(2.1.2) defines the force field potential energy of system the force as the derivative of this potential relative to position. The meaning of the right side is 1st term - is the energy between covalently bonded atoms. this length, it becomes increasingly poor as atoms separate. 2nd term- is energy due to geometry of electron orbitals involved in covalent bonding. 3rd term- it represents the energy for twisting a bond due to bond order and neighbouring bond or lone pair of electrons.

One bond have move then one of these terms such that total torsional is expressed as a fouriers series. 4th term- is the non bonded energy between all atoms pairs which can be decomposed into van der waals and electrostatic energy. van der waals energy is calculated using the equilibrium distance r_{oij} and well depth. The factor of $2r_{oij}$ the energy is sometimes given in terms of r where $r_{oij} = 2^{\frac{1}{\sigma}}\sigma$ the electrostatics energy uses hear assume that charged due to proton and electron in an atom can be represented by a single point charge. Molecular Mechanics is computational methods that computes potential energies surface for particular arrangement of atom using potential function that are derived using classical physics. Molecular Mechanics energy expression consist of a simple algebraic equation for energy of compound it does not use wave function or total electron density. A set of equation with their associated constant is called force field. The constant in this equation are obtained from spectroscopic data or ab initio calculation.

The fundamental assumption of the molecular mechanics is the transfer ability of parameter. This gives a very simple calculations that can be applied to very large molecular systems. The performance of the technique is dependent on four factor.

1.The functional form the energy expression.

2.The data used to parameterize the constant.

3.The technique used to optimized the constant from the data.

4.The ability of the users to apply the technique in a way consistent limits strengths and weaknesses.

In order for the transfer ability of parameters to be a good description of the molecule, force field uses atom type. This means that a sp^3 carbon will be described by different parameters than a sp^2 atom. Some force fields even parameterized atom for specific functional groups.

For eg: The carbonyl oxygen in a carboxylic acid may be described by different parameters than the carbonyl in ketone. The energy expression consist of the sum of simple classical equation. These equation describe various aspect of the molecule such as bond stretching, bond bending, torsion electrostatic interaction, van der waals forces and hydrogen bonding. force field differ in the number of terms in energy expression. the complicity of those term and the way in which the constant were obtained since electron are not explicitly included electronic processes cannot be modeled. Terms in the energy expression that described a single aspect of the molecular shape such as bond stretching, angle bending, ring inversion or torsional motion are called balanced term. All force field have atleast one valence term and most have 3 or more. Terms in the energy expression that describes how one motion of the molecule affects another are called cross terms. A cross term commonly used is a stretch bond term, which describe how equilibrium bond lenghth tend to shift and bond angles are change. Some force fields have no cross term and may compensate for this by having sophisticated electrostatic function[**?**].

Some of the commonly used forcefield in molecular mechanics are AMBER, CHARMM, CFF, CHEAT, DREIDING, ECEPP, EFF, GROMOS, MM1, MM2, MM3, MM4, MMFF, MOMEC, OPLS, Tripos, UFF, YETI and so on.

AMBER is an assisted model building with energy refinement and was parameterized specifically for proteins and nucleic acid. It uses only five bonding and anti-bonding term with sophisticated electrostatic treatment[**?**].

CHARMM is an chemistry at Harvard macromolecule mechanics is the name for both a forcefield and program incorporating that forcefield. It was originally devised for proteins and nucleic acid. It is applied to wide range of application like biomolecules, molecular dynamics, solvation, crystal packing vibrational analysis and also QM/MM studies. It uses five valence terms, on of which is an electrostatic term[**?**].

CFF is the consistent force field which developed to yield consistent accuracy of results for conformations, strain energy, vibrational spectra and vibrational enthalpy of proteins[**?**].

CHEAT is carbohydrate hydroxyl represent by external atoms devised specially for modeling carbohydrates[**?**].

DREIDING is devised for organic or bio-organic molecule forcefield used for large biomolecular system. It uses five valence terms, one of which is an electrostatic term[**?**].

UFF stands for Universal forcefield widely used for system containing inorganic elements. It uses four valence term but not an electrostatic term[**?**].

MM1, MM2, MM3, MM4 are general purpose organic force fields. MM3 method is one of the most accurate modelling hyddrocarbon, These forcefields use five to six valence terms, one of which is an electrostatic term and one to nine cross term[**?**].

OPLS stands for optimized potential for lquid simulation was developed for modeling bulk liquids[**?**].

2 Hartree fock theory

The many-electron system is very complex andnit requires elaborate computational methods. Conceptually and computational simplification can be obtained by introducing independent-particle models, where the motion of one electron is considered to be independent of the dynamics of all other electrons. An independent-particle model means that the interactions between the particles is approximated, either by neglecting all but the most important one or by taking all interactions into account in an average fashion. Within electronic structure theory, only the latter has an acceptable accuracy, and is called Hartree–Fock (HF) theory. In the HF model, each electron is described by an orbital and the total wave function is given as a product of orbitals. Electrons are indistinguishable fermions and its overall wave function must be antisymmetric, which is conveniently achieved by arranging the orbitals in a Slater determinant. The best set of orbitals is determined by the variational principle, that is the HF orbitals give the lowest energy within the restriction of the wave function being a single Slater determinant. The shape of a given molecular orbital describes the probability of finding an electron, where the attraction to all the nuclei and the average repulsion to all the other electrons are included. Since the other electrons are described by their respective orbitals, the HF equations depend on their own solutions, and must therefore be solved iteratively. The molecular orbitals then expanded in a basis set of which resulting equations are written as a matrix eigenvalue problem. The elements in the Fock matrix correspond to integrals of one and two electron operators over basis functions, multiplied by density matrix elements. The HF equations in a basis set obtained by repeated diagonalizations of a Fock matrix. The HF model is considered to be a branching point where either additional approximations can be invoked resulting to semi-empirical methods, or by adding additional determinants it can be improved to generate models that can be made to converge towards the exact solution of the electronic Schrödinger equation. Semi-empirical are the methods which derived from the HF model by neglecting all integrals involving more than two nuclei in the construction of the Fock matrix. HF model limited accuracy therefore such approximations will lead to a poor model. Semi-empirical methods relies on turning the remaining integrals into parameters and fitting these to experimental data, especially molecular energies and geometries. Such methods are computationally much more efficient than the ab initio HF method, but are limited to systems for which parameters exist. HF theory gives average electron–electron interactions but neglects the correlation between electrons. Methods that include electron correlation require a multi determinant wave function, since HF is the best single-determinant wave function. Multideterminant methods are computationally much more involved than the HF model, but can generate results that systematically approach the exact solution of the Schrödinger equation. Density Functional Theory (DFT) in the Kohn–Sham version can be considered as an improvement on HF theory, where the many-body effect of electron correlation is modeled by a function of the electron density. DFT is, analogously to HF, an independent-particle model and is comparable to HF computationally, but provides significantly better results. The main disadvantage of DFT is that there is no systematic approach to improving the results towards the exact solution[?].

3 Basis set

Basis set is one of the approximation introduced in all ab initio method. Unknown function, such as a molecular orbital (MO), in a set of known functions is not an approximation if the basis set is complete. Complete basis set means that an infinite number of functions must be used, which is impossible in actual calculations. An unknown MO can be thought of as a function in the infinite coordinate system spanned by the complete basis set. When a finite basis set is used, only the components of the MO along those coordinate axes corresponding to the selected basis functions can be represented. The smaller the basis set, the poorer the representation. The type of basis functions used also influence the accuracy. The better a single basis function is able to reproduce the unknown function, the fewer basis functions are necessary for achieving a given level of accuracy. Knowing that the computational effort of ab initio scales formally as at least M_{basis}^4 it is of course of prime importance to make the basis set as small as possible, without compromising the accuracy. The expansion of the molecular orbitals leads to integrals of quantum mechanical operators over basis functions, and the ease by which these integrals can be calculated also depends on the type of basis function. In some cases the accuracy-per-function criterion produces a different optimum function type than the efficiency-per-function criterion. basis function is a specific type of mathematical function, while a basis set is a collection of basis functions containing a specific set of parameters. The basis set desiderate can be listed as follows: 1. The basis functions should reflect the nature of the problem to obtain good accuracy by a relatively small number of functions. 2. The basis functions should be able to generate a complete basis set, such that a well-defined basis set limit can be obtained. 3. Basis sets should be available in several hierachical levels, where each level provides a well-defined accuracy and the hierachy systematically converges the result towards the basis set limit. Ideally the basis set convergence should be monotomic and fast. 4. For a given accuracy, the basis set should be as computationally efficient as possible, that is delivering the target accuracy for as low a computational cost as possible. The computational cost is often related to the number of basis functions, but other factors may also be important. 5. Basis sets should ideally be universal, that is suitable for different methods (HF, DFT, electron correlation methods, relativistic methods) and different properties (energy, molecular structure, vibrational frequencies, polarizabilities, NMR spin–spin coupling constants, etc.). 6. Be available for all atoms, or at least for a large fraction of the periodic table.

4 Quantum mechanics(QM)

Quantum Mechanics(QM) is the methamethical description of the behaviour of electron and thus of chemistry. in theory, QM can predict any property of an individual atom or a molecule exactly. In practice, the QM equations have only been solved exactly for one electron systems. The QM were devised by Schrödinger and Heisenberg.

The Schrödinger equation is

$$\hat{H}\psi = E\psi \tag{2.4.3}$$

where, $\hat{H}$is the Hamiltonian operator, ψ is a wave function, **E** is the energy. an equation of this form is called an Eigen function. psi is called the Eigen function and E is Eigen value. The wave function ψ is a function of the electron and nuclear position and it can be described the probability of electron being in certain location, but it cannot predict exactly where the electrons are located. The wave function is also called a probability amplitude because it is a square of the wave function that yields probabilities in order to obtain a physical relevant solution of the Schrödinger equation, the wave function must be continuous, single value, normalisable and antisymmetric with respect to the interchange of electron[**?**]. **The Hamiltonian operator $\hat{H}$ is**

$$\hat{H} = -\sum_{i}^{particles} \frac{\nabla_i^2}{2m_i} + \sum_{i<j}^{particles} \sum \frac{q_i q_j}{r_{ij}} \tag{2.4.4}$$

$$\nabla_i^2 = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \tag{2.4.5}$$

Where, ∇_i^2 is the laplacian operator acting on particle i.

m_i is mass of the particle i.

q_i is charge of the particle i.

r_{ij} is the distance between particle.

First term gives the Kinetic Energy of the particle within a wave function.

Second term is the energy due to coloumbic attraction or repulsion of particles.

this equation is time dependent.

Born Oppenheimer Approximation is given by

$$\hat{H} = -\sum_{i}^{electrons} \frac{\nabla_i^2}{a} - \sum_{i}^{nuclei} \sum_{j}^{electrons} \frac{z_i}{r_{ij}} + \sum_{i<j}^{electrons} \sum \frac{1}{r_{ij}} \tag{2.4.6}$$

First term is Kinetic energy of the electrons only.

Second term is the attraction of electrons to nuclei.

Third term is the repulsion between electrons. Various computational methods have strength and weaknesses. Quantum mechanics computes many properties and model chemical reactions whereas molecular mechanics is able to compute very large compound very quickly. It is possible to combine these two methods into one calculation which models a very large compounds using Molecular mechanics and crucial section of the molecule using Quantum mechanics thus these calculation give results faster when only one region needed to be modeled quantum mechanically. It can also be used to model a molecule surrounded by solvent molecules. This type of calculation is called QM/MM calculaion[**?**].

5 Density Functional Theory

Density Functional Theory (DFT) is the method where the energy of the molecule can be determined from the Electron density. In this formulation, the electron density is expressed as a Linear combination of basis functions similar in mathematical form to HF orbitals. A determinant is then formed from these functions, called kahn-sham orbitals. It is the electron density from this determinant of orbitals that is used to compute energy. Kahn-sham orbitals describe the behaviour of electron in molecule. A density functional is then used to obtain the Energy for the electron density. A functional is a function of function, in this case, the electron density. The exact density functionals is not known some of these functionals were developed from fundamental quantum mechanics and some were developed by parameterizing functions. DFT tend to classified either as an ab initio and semi empirical method or in a class by itself. The advantage of using electron density is that the integral for coloumbic repulsion need be done only over the electron density, which is three dimensional function. At least same electron correlation can be included in the calculation.This results in faster calculation than HF Calculations and computations that are more accurate as well. The better DFT functionals give results with an accuracy similar to that of an MP2 Calculation. Density functionals can be broken down into several classes. The simplest is called Xα method. This types of calculation include electron exchange but not correlation. It was introduced by J.C.Slater. The Xα method is similar in accuracy to HF and sometimes even better. LDA is known to give less accurate geometries and predict binding energies significantly too large. The simples approximation is based on electron density, called a local density approximation (LDA), for high spin system, this is called the local spin density approximation (LSDA). LDA calculation have been widely for band structure calculation. Their performance is less impressive for molecule calculation. A more complex set of functionals utilizes the Electron density and its gradient. These are called gradient corrected methods. There are also hybrid methods that combine functionals from other methods with Hartree-fock calculation, usually the exchange integrals. In general, grandient corrected or hybrid calculation give the most accurate results. Recent development in DFT Is the advent of linear scaling algortihm. These algorithms replace the coloumbic terms for distant regions if the molecule with multiple of Expansions This results in a method with a time complexity of N for sufficiently large molecules. The most common scaling techniques are the fast multiplot method (FMM) and the continuous ast multiplot method(CFMM). DFT is generally faster than Hartree-fock for system with more than 10-15 non hydrogen atoms, depending on the numeric integral accuracy and basis set. The linear scaling DFT Method can be fastest ab initio method for large molecules.

6 Band theory

Band structure is one of the most important concepts in solid state physics. It provides the electronic levels in crystal structures, which are characterized by two quantum numbers, the Bloch vector **k** and the band index **n**. Bloch vector is an element of the reciprocal space (in units 1/length)) and the energy of the electron $E_n(k)$he other electrons, which are considered to provide a fixed background (called mean-field). This entirely neglects correlations between the kinetics of the single electron and the others, and thus only serves as an approximation for the complex many-particle physics scenario. However, this is rather good for many purposes, in particular if more complicated potentials are used as justified within density functional theory. The formation of energy bands in semiconductors and by extension insulators can be explained in an analogous manner to metals. The difference being that in semiconductors (insulators) there is an energy gap between the filled valence band and the empty conduction band. **Band formation in semiconductors**. energy band formation in Si semiconductor Si has an atomic number of 14 and the electronic configuration is $1s^2 2s^2 2p^6 3s^2 3p^2$ shown in below diagram.

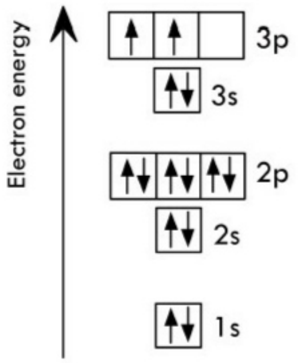
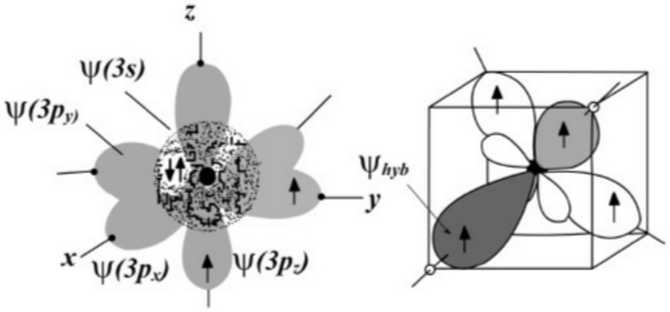


Figure 2.1: Electronic configuration of Si atom. The 3s and 3p together forms the outer shell while the others form the inner shells

The $3s^2 3p^2$ forms the outer shell,the inner shells $1s^2 2s^2 2p^6$ are not considered for electrical conductivity. The 3s and 3p orbitals in Si are having considerably same energy and can hybridize to form sp^3 orbitals. Given that there are 4 electrons a total of 4 sp^3 hybrid orbtials are formed. These form 4 bonds that are directed along the corners of a tetrahedron, as shown in figure below.



(a) Isolated Si

(b) Si just before bonding

Figure 2.2: (a) Isolated Si atoms showing the outer shell orbitals. (b) In a solid, these orbitals hybridize to form 4 sp 3 orbitals, just before bonding.

Hybridization is a common property of elements of Group IV of the periodic table to which Si belongs to. C which is in top of the group can form a variety of hybrid orbitals (sp^3, sp^2, sp). Both Si and the element below it, Ge, can form sp^3 hybrid orbitals. Sn and Pb (below Ge) are metals with low melting points. In the case of Si, the hybrid orbitals interact the same way that atomic orbitals interact in metals. Consider a bond formed between 2 sp^3 hybrid orbitals (1 from each Si atom). The two orbitals can interact to form a bonding () and anti-bonding ($*$) orbital. Since each Si atom will contribute one electron to the bond there will be a total of 2 electrons which will both go to the bonding orbital. Thus, each Si atom can form a bond with 4 other Si atoms and in all cases the bonding orbital () will be full. A solid will be formed from a large number of these orbitals. When the bonding orbitals interact they will form an energy band, called valence band. This valence band will be completely full since the bonding orbital is full. Similarly, the anti-bonding orbitals can interact to form an energy band, called conduction band. This will be completely empty. Unlike metals, the valence and conduction band in a semiconductor is separated by a forbidden energy gap, this is called **band gap**. The formation of bands in Si crystal is given below figure

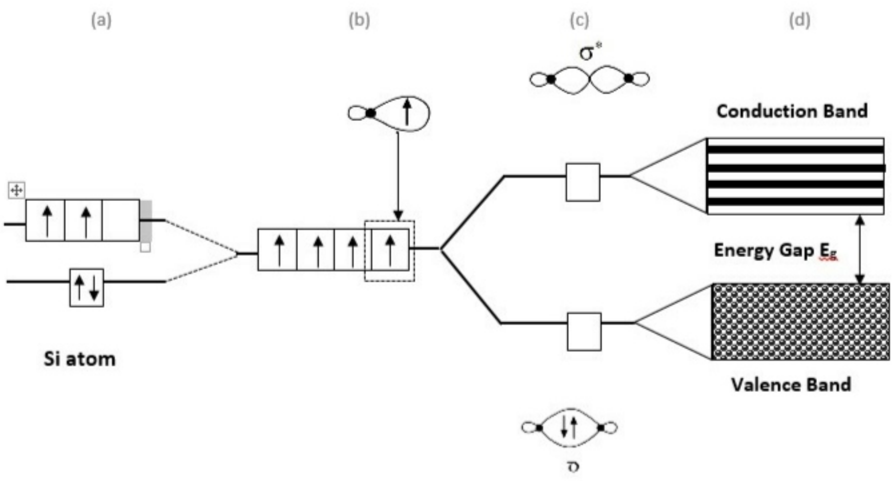


Figure 2.3: Formation of energy bands in Si. (a) Si atom with 4 electrons in outer shell form (b) 4 sp 3 hybrid orbitals. (c) The hybrid orbitals form and ∗ orbitals. (d) These orbitals overlap in a solid to form the valence and conduction band

Si has band gap (E_g) value of 1.11 eV at room temperature (300 K). The formation of a band gap (filled valence band and empty conduction band with a forbidden energy gap) can be extended to other semiconductors and insulators.

6.1 A simple one-dimensional example

electron in the potential is given by

$$V(x) = 2Ucos(gx) = U(e^{igx} + e^{-igx}) \tag{2.6.7}$$

where,$g = \frac{2\pi}{d}$

As V(x+d)=V(x) for all x the potential exhibits the period d and can be thought as the potential resulting from a lattice of ions. by solving Schrödinger equation

$$\hat{H}\psi = E\psi \tag{2.6.8}$$

with the Hamilton operator

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x) \tag{2.6.9}$$

To normalize wave functions, we consider a finite crystal with N periods and use periodic boundary conditions $\psi(x + Nd) = \psi(x)$. Then the wave function can be expanded in a discrete Fourier series

$$\psi x = \sum_q a_q e^{iqx} \tag{2.6.10}$$

where , q is an integer multiple of $2\pi/Nd$. At a later stage we allow N to become arbitrarily large, so that the artificial periodicity does not matter and the spacing of q values becomes infinitesimal small. Inserting into the Schrödinger equation

$$\sum_{q}\left(\frac{\hbar^2 q'^2}{2m}e^{iq' x}+Ue^{i(q'+g)x}+Ue^{i(q'-g)x}\right)a_{q'}=E\sum_{q'}e^{iq' x}a_{q'} \tag{2.6.11}$$

Multiplying both sides with e^{iqx}/Nd and performing the integral $\int_{-Nd/2}^{Nd/2}dx$ Resulting equation is

$$\frac{\hbar^2 q^2}{2m}a_q+Ua_{q-g}+Ua_{q+g}=E\sum_{q'}e^{iq' x}a_{q'} \tag{2.6.12}$$

This shows that Fourier components with different q couple to each other if their difference matches g. This class can be uniquely described to be all the values q which can be written as $q=k+lg(k)$ with l ∈ Z, where k is a fixed value in the interval $-\pi/d<k\leq\pi/d$. Setting $a_{k+lg}=a_l^{(k)}$ we find for each k an infinite set of equations

$$\frac{\hbar^2(k+lg)^2}{2m}a_l^{(k)}+Ua_{q-g}+Ua_{q+g}=E\sum_{q'}e^{iq' x}a_{q'} \tag{2.6.13}$$

[?]

for l = . . . , −2, −1, 0, 1, 2, . . .

6.2 Bloch functions

The Schrödinger Equation is given by

$$\nabla^2\psi(r)+\frac{2m_o}{\hbar^2}[E-V(r)]\psi(r)=0 \tag{2.6.14}$$

where, r is position, ψ is the Bloch wave, u is a periodic function with the same periodicity as the crystal, the wave vector k is the crystal momentum vector, e is Euler's number

writing

$$u_k(r)=e^{-ik.r}\psi_k(r) \tag{2.6.15}$$

we have,

$$u_k(r+R_i)=exp[-ik(r+R_i]\psi_k(r+R_i)=e^{-ik.r}\psi_k(r)=u_k(r) \tag{2.6.16}$$

that is $u_k(r)$ has the periodicity of the lattice.

$$\psi_k(r)=u_k(r)e^{ik.r} \tag{2.6.17}$$

The one-electron wave functions is perfect crystals are the product of a plane wave by a function which has the periodicity of the lattice. Such a wave function is called a Bloch function.

Bloch functions are generally normalised in a unit cell of the crystal, or they may be normalised in unit volume, or in the parallelepiped used for the periodic boundary conditions. In this parallelepiped the Bloch functions form an orthogonal system.

It can be proved that the Coulomb and exchange integrals computed with Bloch functions have the correct periodicity. Hence the use of the Bloch theorem as a boundary conditions is self-consistent.

The vector k plays the role of a set of three quantum numbers.

$$\psi_k(r) = e^{ik.r} \tag{2.6.18}$$

with $E(k) = \hbar^2 k^2/2m.\hbar k$ is in this case just the momentum of the electron. It is not however an eigenvalue of the operator-$i\hbar\nabla$ and is not equal to the average value of the momentum of the electron in state k. We have seen that k is a constant of the motion, that is the electron in state k is not scattered at all into other states by a perfect lattice. It is clear that E is a function of k and may be considered as a continuous function, though for some values of k it may not be differentiable, and a particular dispersion relation E(k) characterises each band.

Detailed knowledge of the band structure is becoming more and more essential in the design of semiconductor devices, such as a tunned diodes, Gunn oscillators, injection lasers, infrared detectors and other devices which depend on peculiar characteristics of the energy bands for their operation.

This is in contrast to the development of the transistor which required only the general concepts of the theory.

If now (1.1.1) is substituted into (1.1.4), the equation satisfied by $u_k(r)$is obtained.

$$\nabla^2 u_k + 2ik.\nabla u_k - k^2 u_k + \frac{2m_o}{\hbar^2}[E(k) - V(r)]u_k = 0 \tag{2.6.19}$$

If we wish to write above equation as a eigenvalue equation, we introduce a k-dependent energy operator H(k)operating on $u_k(r)$

$$H(k)u_k(r) = [-\frac{\hbar^2}{2m_o}(\nabla + ik)^2 + V(r)]u_k(r) = E(k)u_k(r) \tag{2.6.20}$$

and we note for future reference that

$$grad_k H_k = -\frac{i\hbar^2}{m_o}(\nabla + ik) \tag{2.6.21}$$

Since$-i\hbar\nabla$ is the operator p, we can write

$$\nabla^2 u_k - \frac{2}{\hbar}k.pu_k + \frac{2m_o}{\hbar^2}[E(k) - \frac{\hbar^2 k^2}{2m_o} - V(r)]u_k = 0 \tag{2.6.22}$$

This equation is used to calculate corresponding to a certain k when E and u are known as a nearby ; the term containing k.p is treated as a perturbation (k.p approximation) If in () we change k in $-k$, we have

$$\nabla^2 u_{-k} - 2ik.\nabla u_{-k} - k^2 u_{-k} + \frac{2m_o}{\hbar^2}[E(-k) - V(r)]u_{-k} = 0 \tag{2.6.23}$$

By comparing above equation with the complex conjugate of () we see that E must be an even function k and u_k mus be a multiple of u_k^*

$$E(-k) = E(k) \tag{2.6.24}$$

$$u_k(r) = Cu_k{}^* r \tag{2.6.25}$$

C being c complex constant of modulus one. This constant can be adjusted to be one, or any chosen phase factor, by adjusting the arbitrary phase of $u_k(r)$. In a similar way it can be proved that, provided the crystal has a center of inversion at the origin,

$$u_k^*(-r) = C^{'} u_k r \tag{2.6.26}$$

$c^{'}$ having the same properties as **C** . The symmetry expressed by these relations does not follow from crystal symmetry. It is known as time reversal symmetry. It may be considered as a analogue, for electron waves, of the optical principle of reversibility of the light path.

Bloch Theorem: For ideal crystals with a lattice-periodic Hamiltonian satisfying $\hbar(r+R) = \hbar(r)$ for all vectors R of the Bravais lattice, a complete set of eigenstates can be written in the form $\psi_{nk}^{(r)} = e^{ikr} u_{nk}(r)$ where $u_{nk(r+R)} = u_{nk}(r)$ is a lattice-periodic function. The corresponding energies E n (k) are continuous functions in the Bloch vector k for each band index n and constitute the energy bands. The Bloch vectors are restricted to the first Brillouin zone and for finite crystals there are as many different Bloch vectors **k** in each band as there are primitive unit cells in the crystal[**?**].

6.3 Pauli principle and Fermi energy

A real crystal contains not only a single electron but typically several electrons per unite cell. Many-particle quantum physics states that valid many-particle states can only be constructed, if one does not allow two electrons to occupy the same single particle level. Thus the ground state of the many-electron system is obtained by subsequently filling the lowest energy levels with electrons. The energy of the level filled with the last electron is called the Fermi energy E_F. In order to determine E_F, we need to count the number of k-values, which is easy for a finite crystal. The first Brillouin zone contains as many k points as there are unit cells in a finite crystal. In this context the spin degree of freedom has to be taken into account. In most cases the energy bands are identical for both spin directions . Thus each state with a given Bloch vector and band index η can accommodate two electrons and consequently each band can take two electron per primitive unit cell. Extended crystals do not allow for a macroscopic net charge due to the Coulomb repulsion. Thus the total number of electrons must match the charges of the nuclei. This rule provides the Fermi energy for a given crystal.

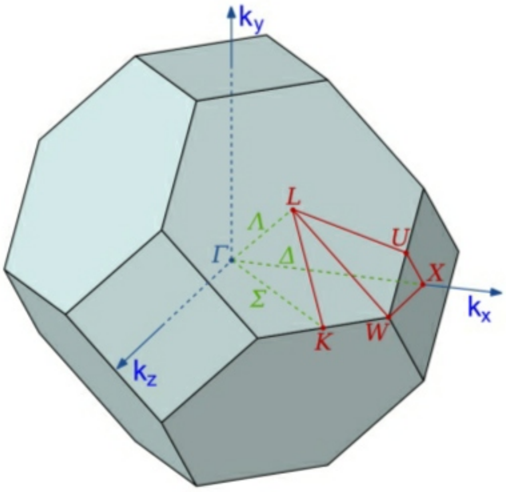


Figure 2.4: Brillouin zone for the fcc lattice

The location of the Fermi energy with respect to the band structure is crucial for the optical and electrical properties of the crystal. If the Fermi energy is located within one band the solid is a metal. If on the other hand the Fermi energy is located in a band gap between the uppermost entirely filled band (the valence band) and the next entirely empty band (the conduction band), the material is either a semiconductor or an insulator (for larger band gaps), where the differentiation is however not sharp. Note that the presence of extra charges, such as replacing some atoms by others with a different nuclear charge (doping) or electric potentials at interfaces (e.g. field effect transistors) allow for a (slight) manipulation of the total number of electrons. While the corresponding change in Fermi energy is negligible for metals, in semiconductors any extra electron occupies the conduction band, while any missing electron provides an empty state (called hole) in the valence band. Thus the conductivity of semiconductors can be easily modified, which is the basis for most electronic applications of these materials.

3

Results and calculation

Cubic and hexagonal semiconduction are the most common structures in which the binary semiconduction crystallize.from the cubic structures, the zinc-blende (zb) is the most common.In this project we present such a theoretical comparison using an an density functional theory using pseudo-potential plane wave function based on the local density approximation (LDA) for the correlation and exchange potentials.In NWChem projected DOS are only perform in the pspw code. The band code only has total DOS. There are differences in how DOS is calculated in pspw and band. In pspw, the DOS is computed by taking a lorentzian distribution about each eigenvalue, whereas in band, a tetrahedral integration over the brillioun zone is used. generalized gradient approximation (GGA) in the scheme of Perdew-Burke-Ernzerhof (PBE) to describe the exchange-correlation functional.In this code, the plane wave functions of valence electrons are expanded in a plane wave basis set, and the use of norm-conserving pseudopotential allows a planen wave energy cutoff E_c. Only plane waves with kinetic energies smaller than E_c are used in the expansion. Reciprocal-space integration over the Brillouin zone is approximated through a careful sampling at finite number of k-points using a Monkhorst-Pack mesh.. We choose the the Brillouin-zone sampling mesh parameters for the k-point set are $9\times9\times9$ for the band structure calculation whereas for the density of state dos-grid is $11\times11*11$. The lattice constant for the given zinc blende structure is given in the following table

Name	Lattice constantA^o	Name	Lattice constantA^o
AlAs	5.662	GaP	5.448
AlP	5.451	GaSb	6.095
AlSb	6.135	GeGe	5.658
AsB	4.777	InAs	6.058
BN	3.616	InP	5.869
BP	4.538	InSb	6.478
CC	3.567	SiC	4.358
CdS	5.818	SiSi	5.431
CdSe	6.077	SnSn	6.46
CdTe	6.481	ZnS	5.406
GaAs	5.653	ZnSe	5.667
GaN	4.52	ZnTe	6.103

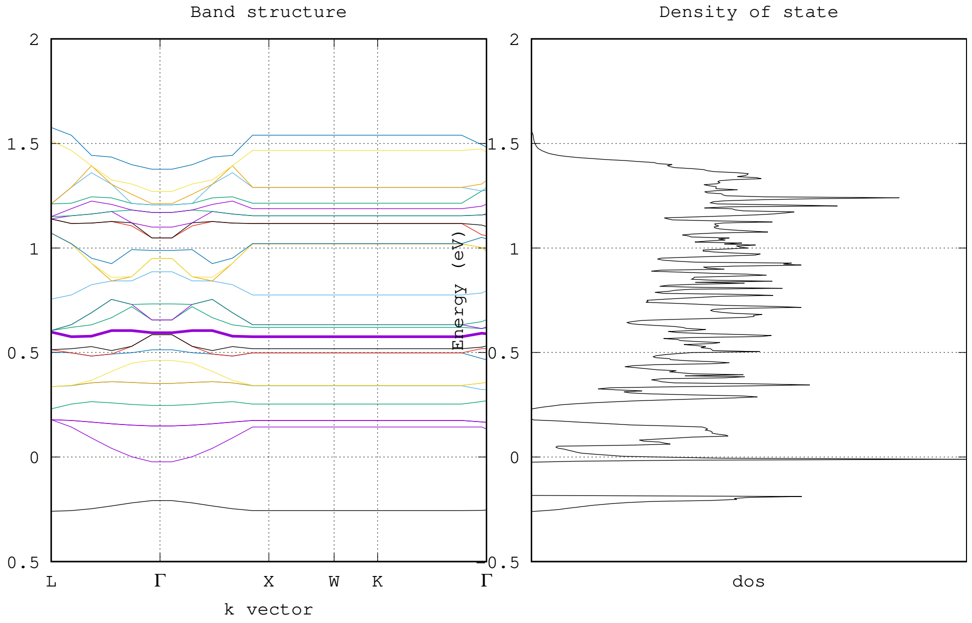


Figure 3.1: The band structure and density of state for Aluminiumarsenide.

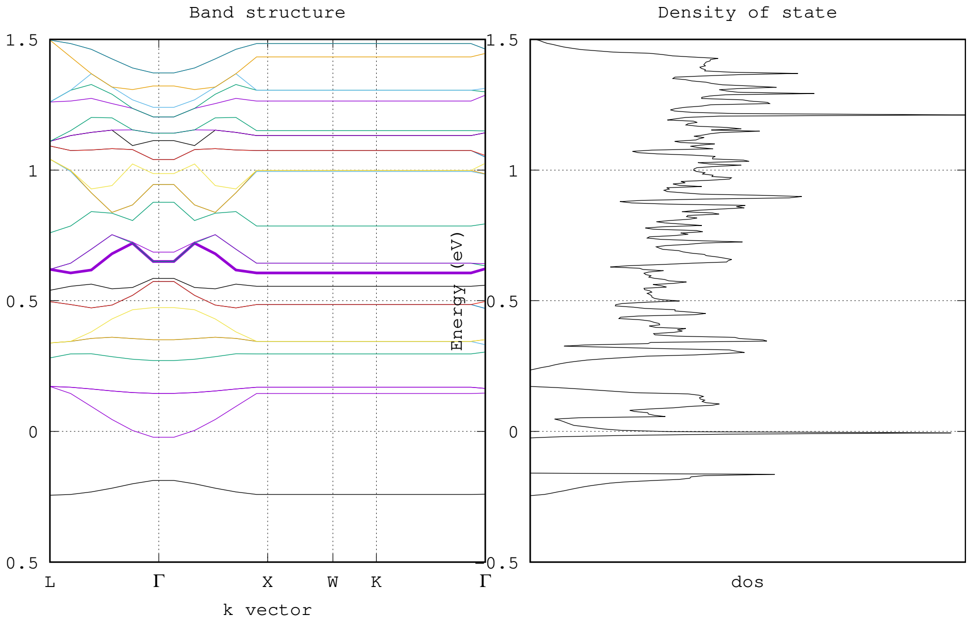


Figure 3.2: The band structure and density of state for Aluminium phosphide

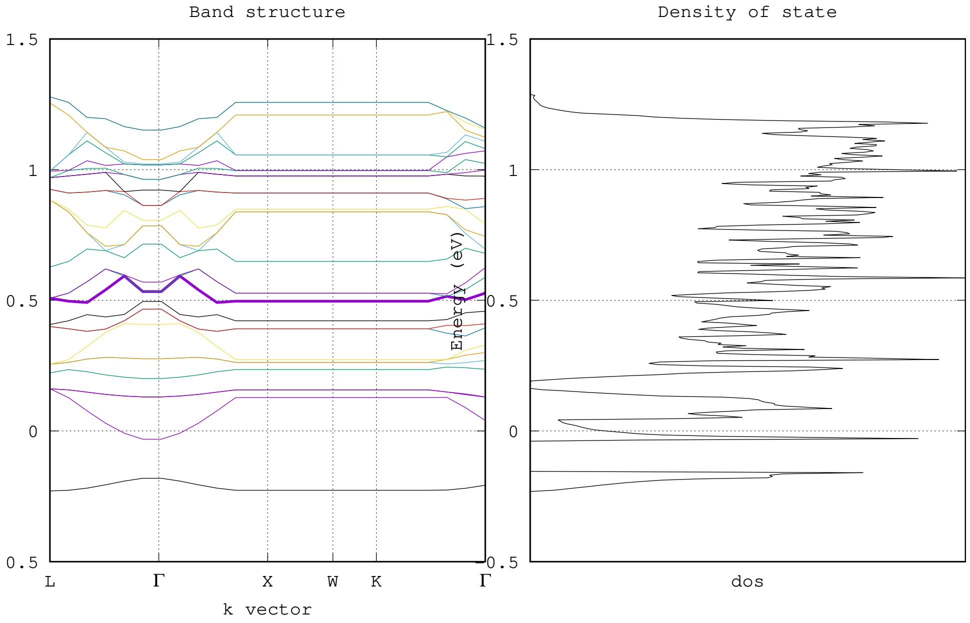


Figure 3.3: The band structure and density of state for Aluminium Antimonide

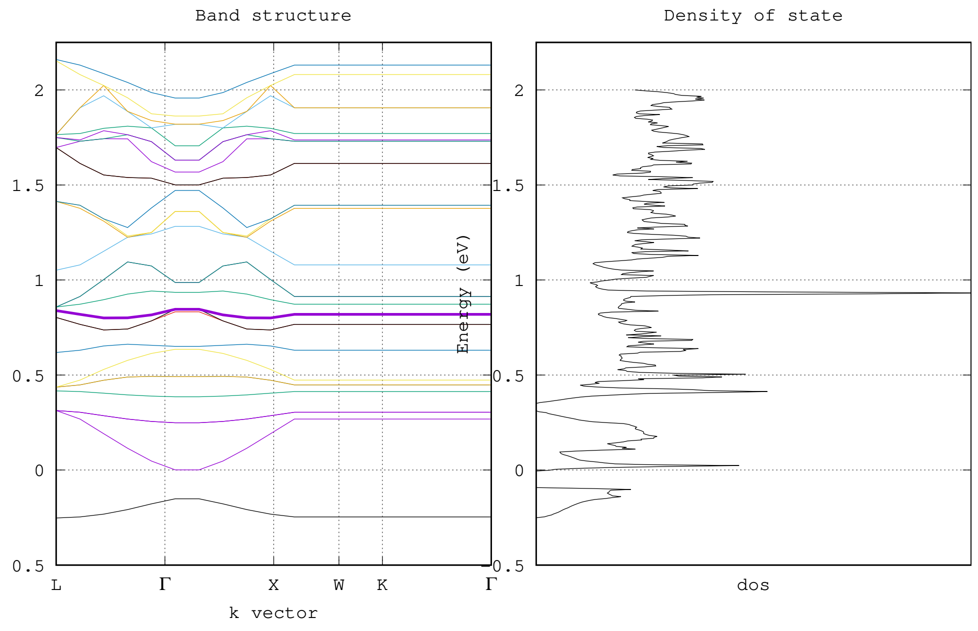


Figure 3.4: The band structure and density of state for Arsenic Boride

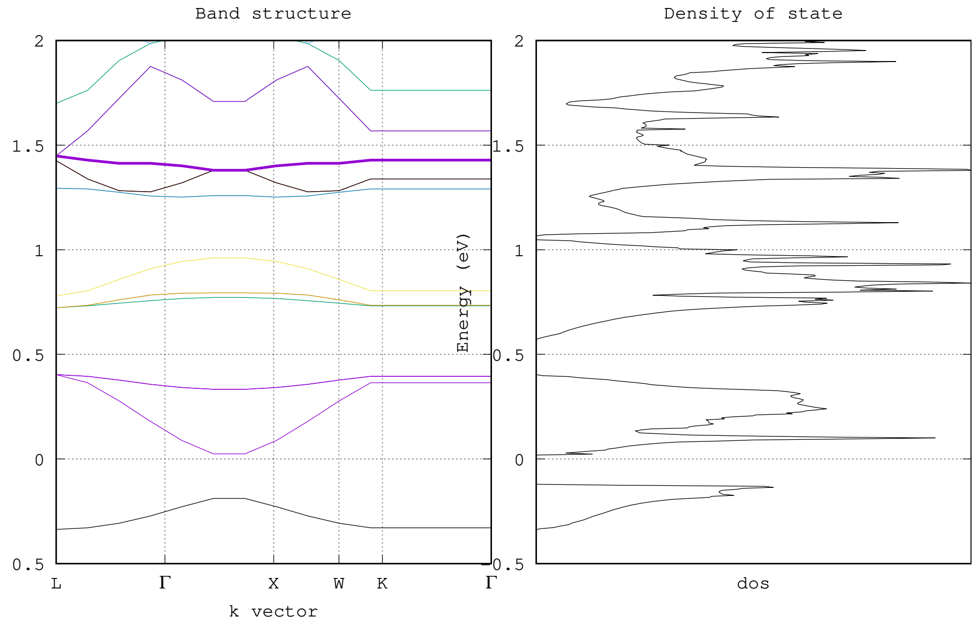


Figure 3.5: The band structure and density of state for Boron Nitride

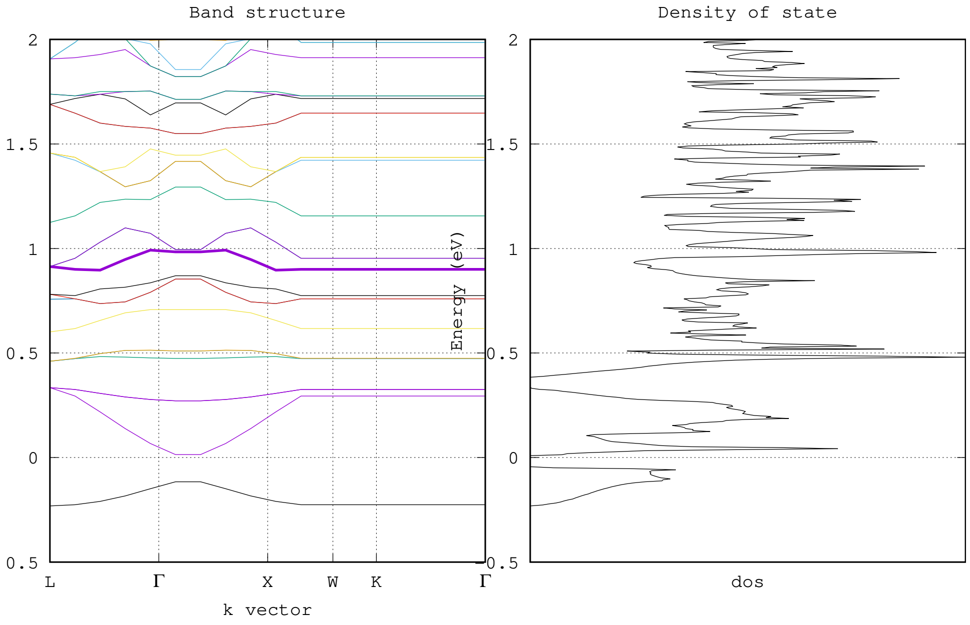


Figure 3.6: The band structure and density of state for Boron Phosphide

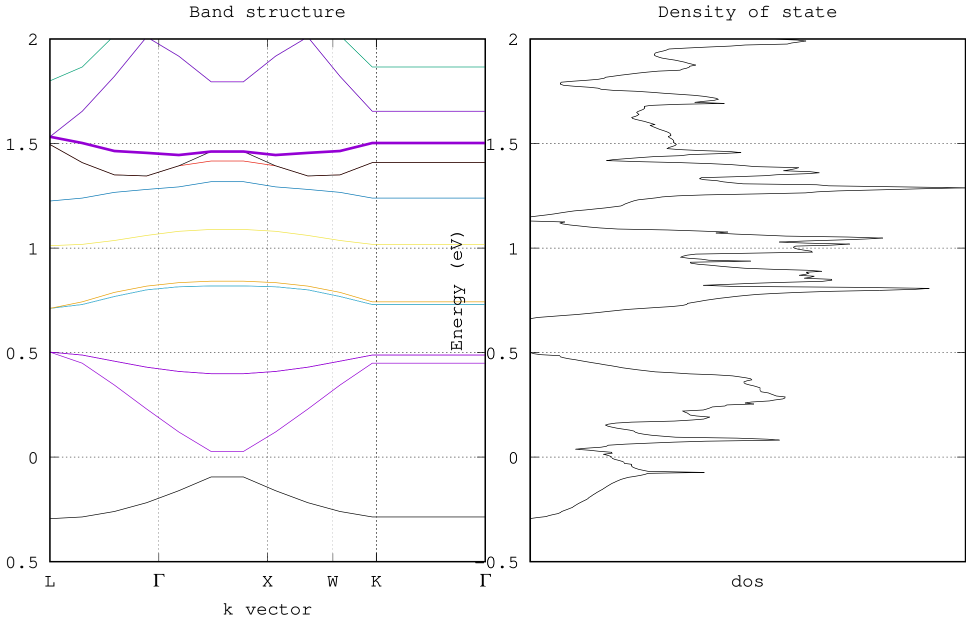


Figure 3.7: The band structure and density of state for diamond.

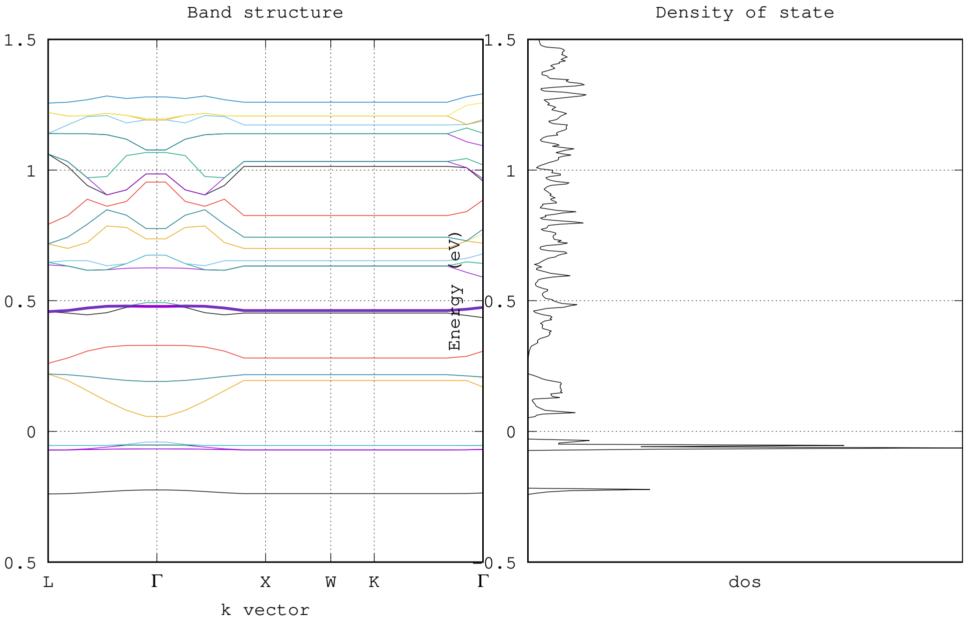


Figure 3.8: The band structure and density of state for Cadmium Sulphide

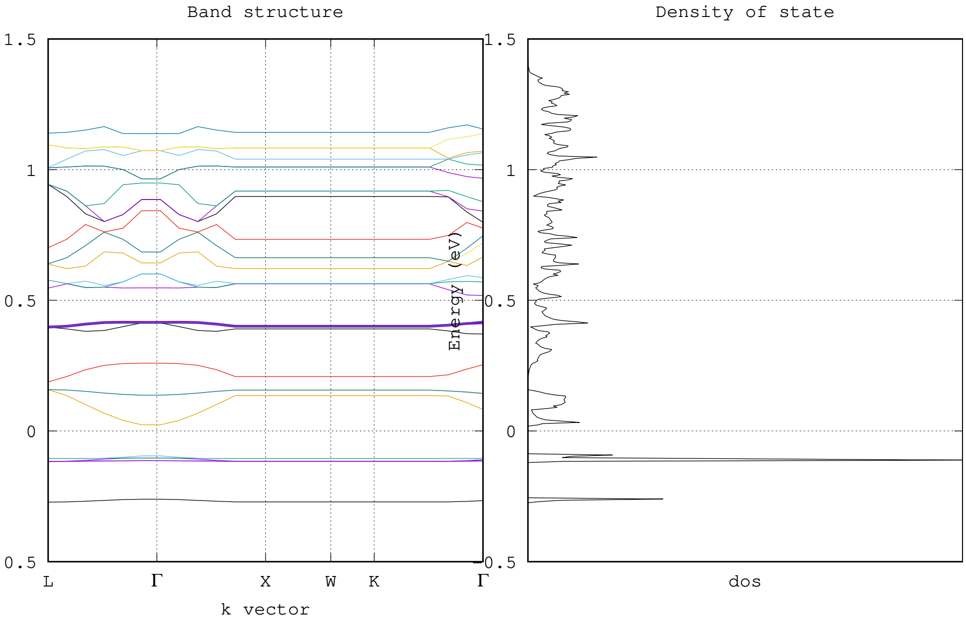


Figure 3.9: The band structure and density of state for Cadmium Selenide

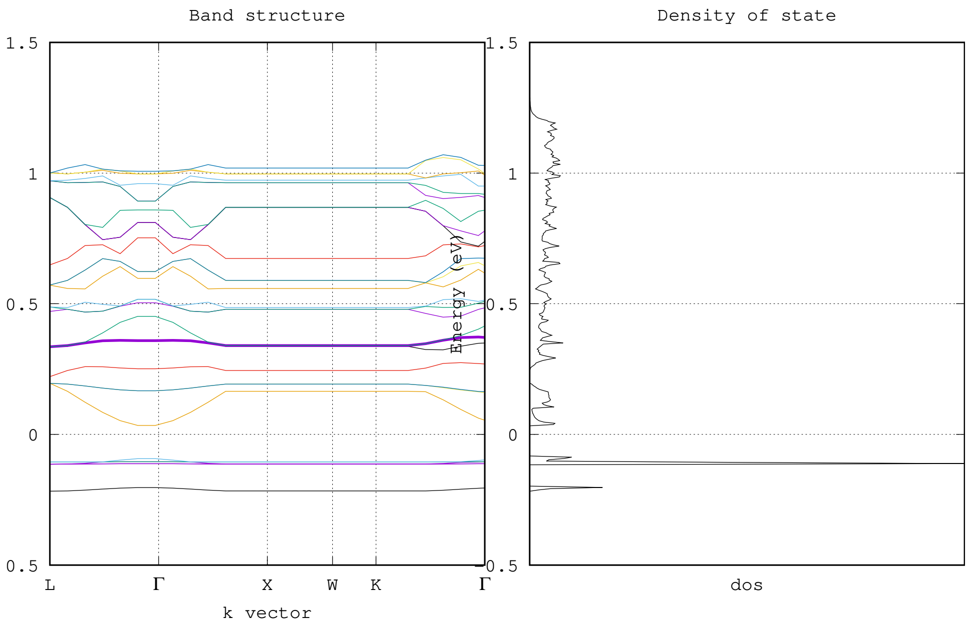


Figure 3.10: The band structure and density of state for Cadmium telluride.

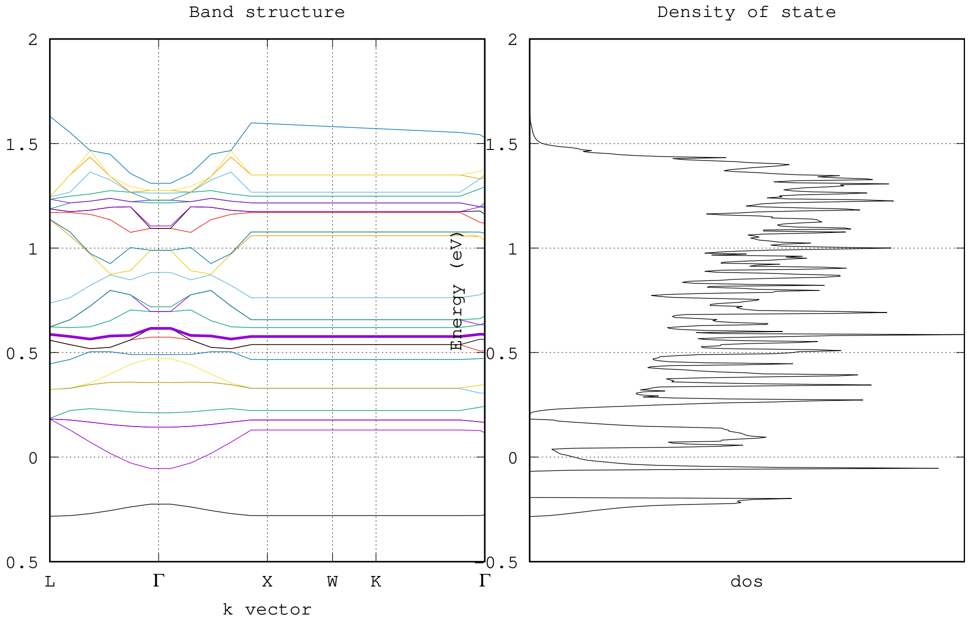


Figure 3.11: The band structure and density of state for Gallium arsenide

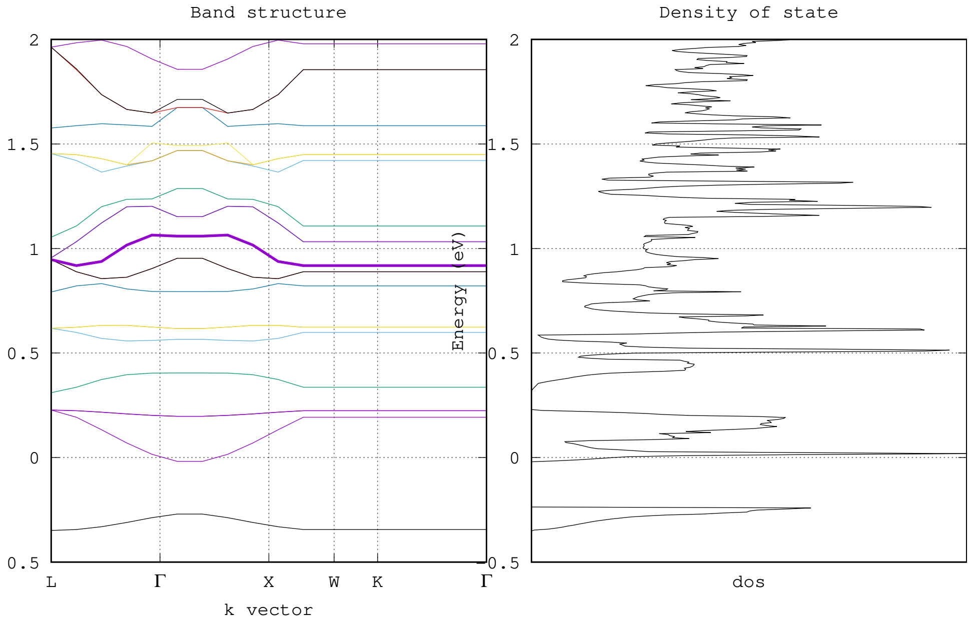


Figure 3.12: The band structure and density of state for Gallium nitride

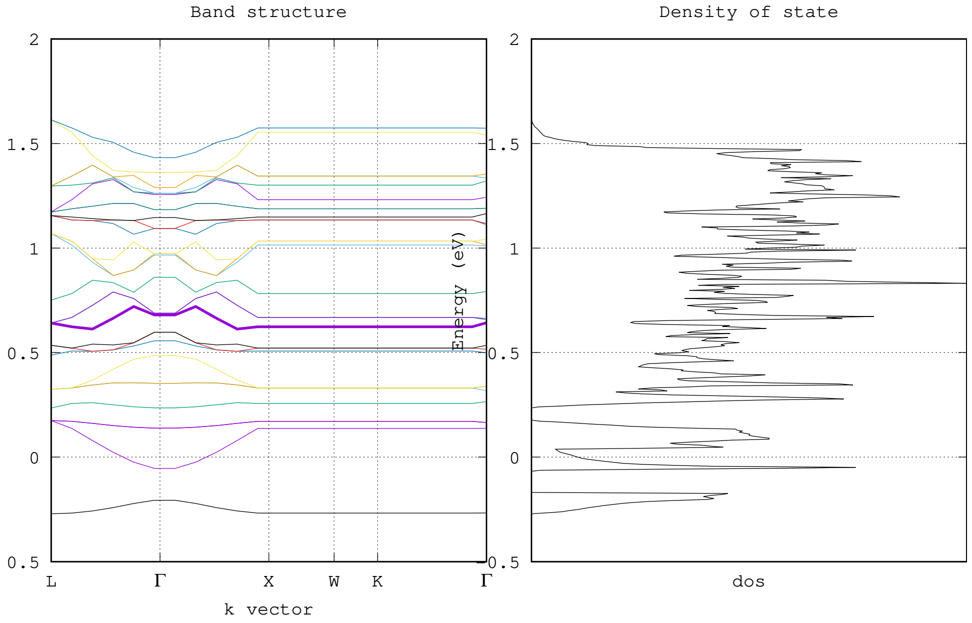


Figure 3.13: The band structure and density of state for Gallium phosphide

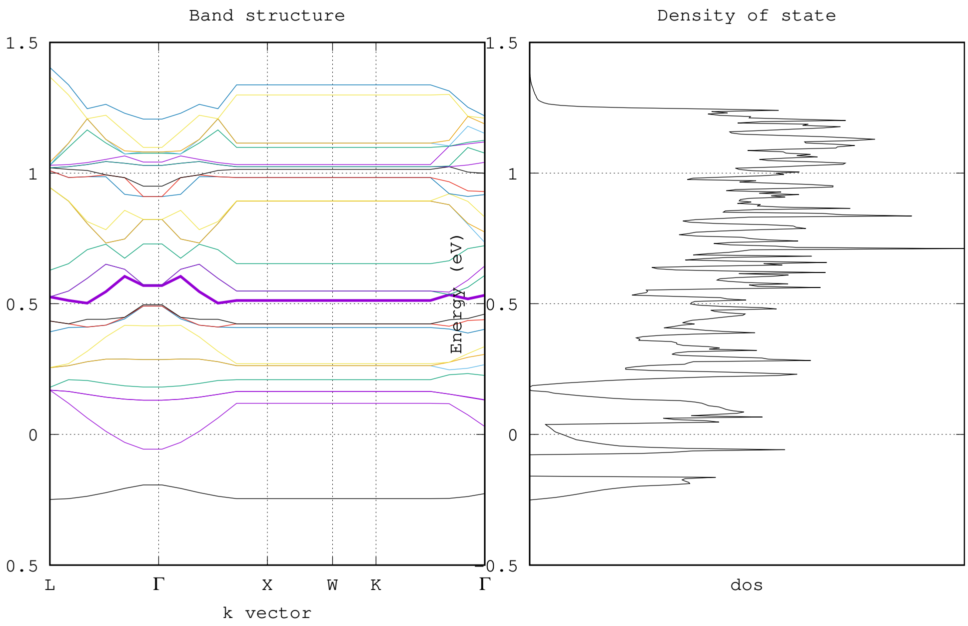


Figure 3.14: The band structure and density of state for Gallium antimonide

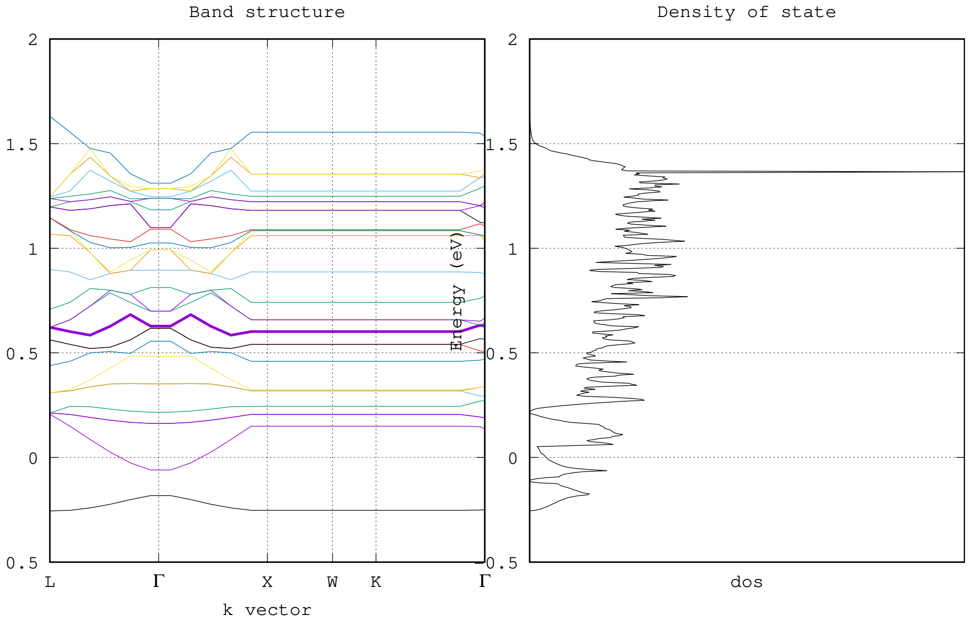


Figure 3.15: The band structure and density of state for Germanium

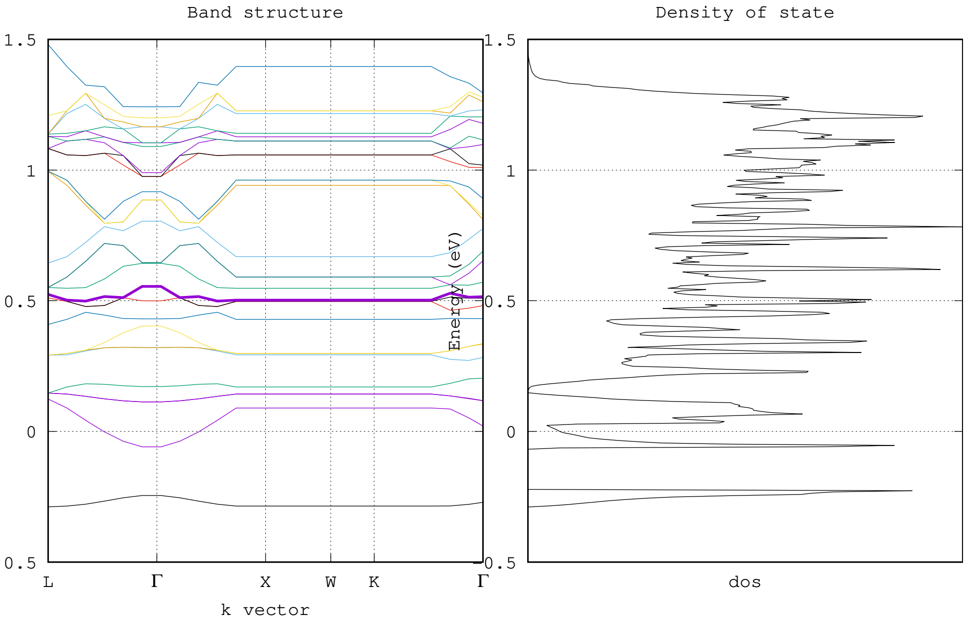


Figure 3.16: The band structure and density of state for Indium arsenide

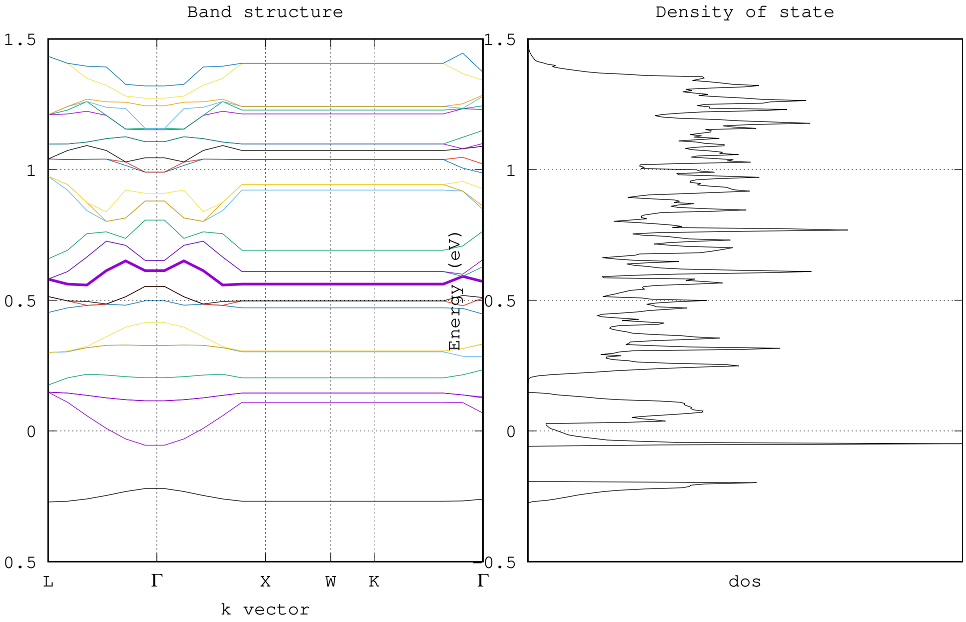


Figure 3.17: The band structure and density of state for Indium phoshide

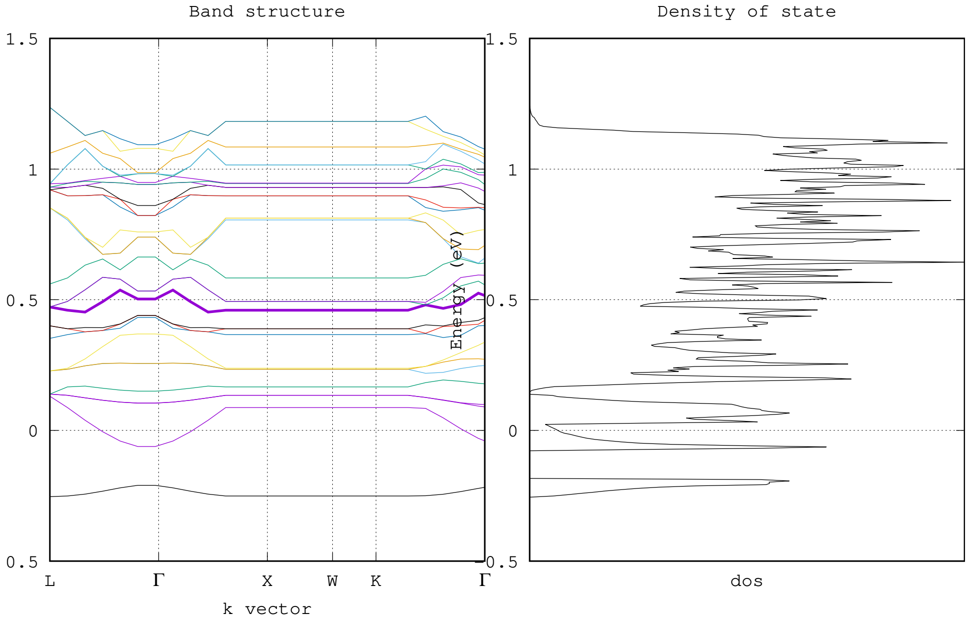


Figure 3.18: The band structure and density of state for Indium antimonide

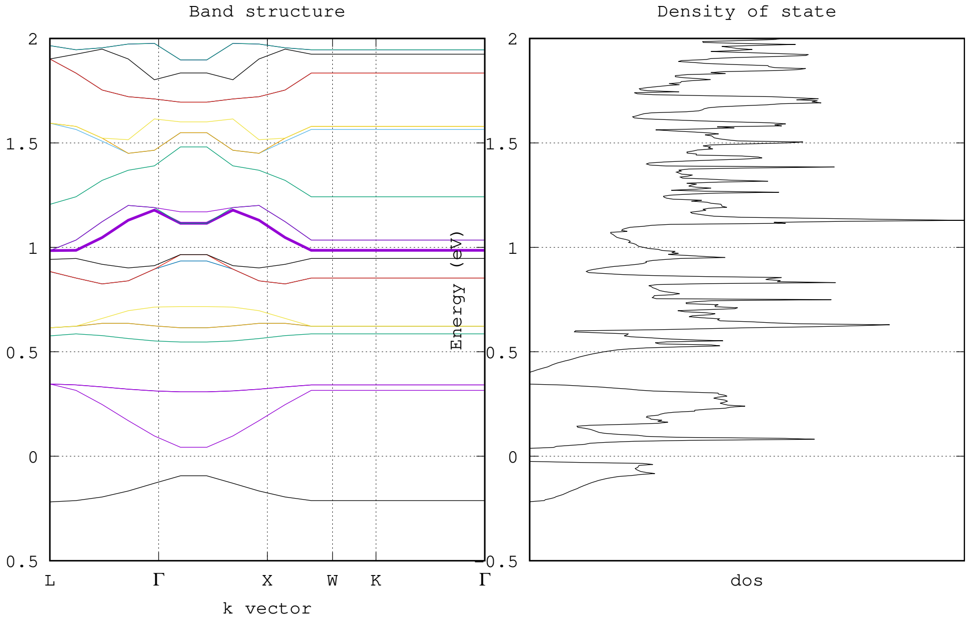


Figure 3.19: The band structure and density of state for Silicon carbide

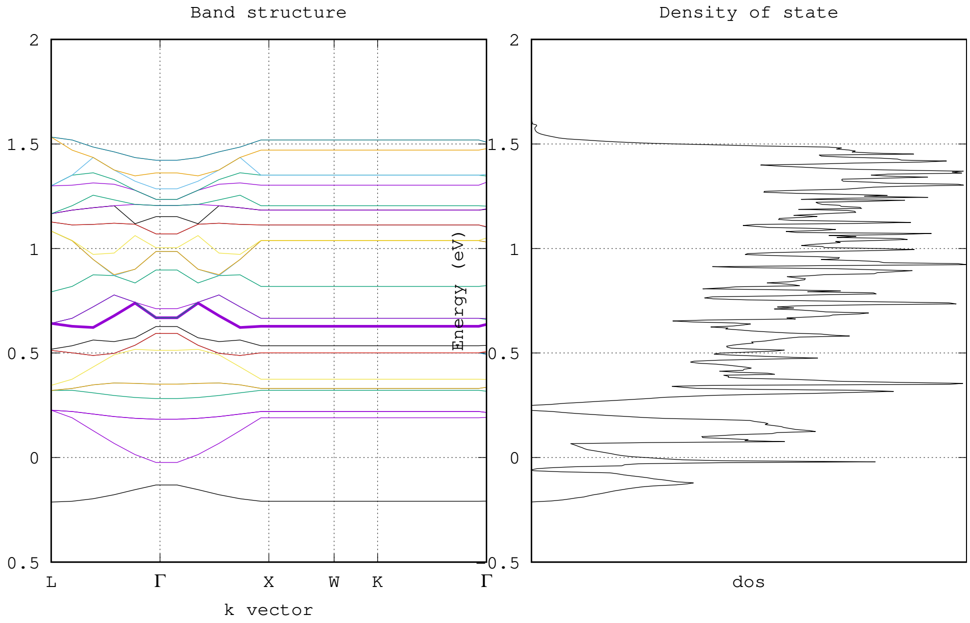


Figure 3.20: The band structure and density of state for Silicon

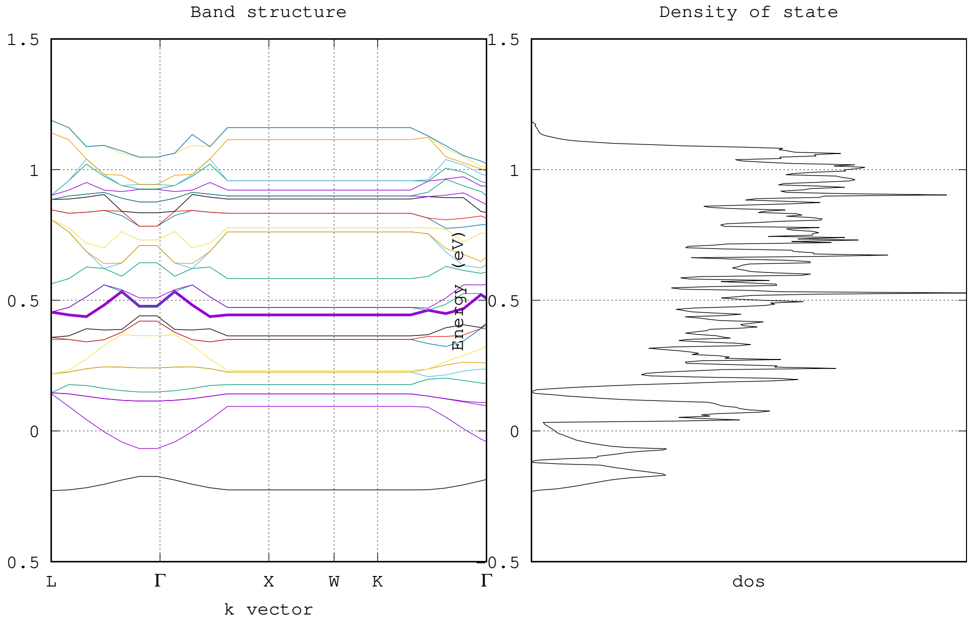


Figure 3.21: The band structure and density of state for Tin

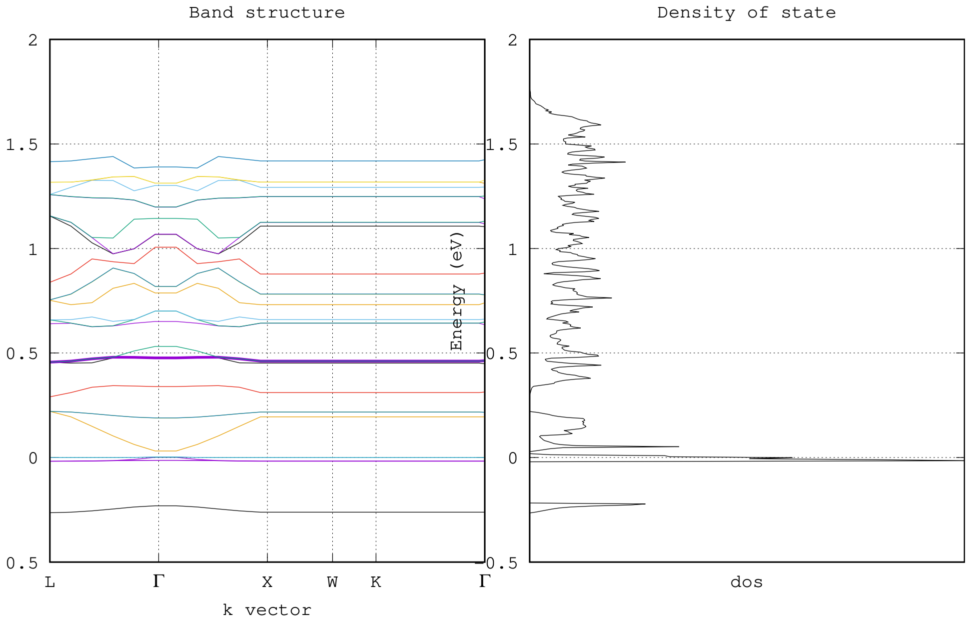


Figure 3.22: The band structure and density of state for Zinc Sulphide

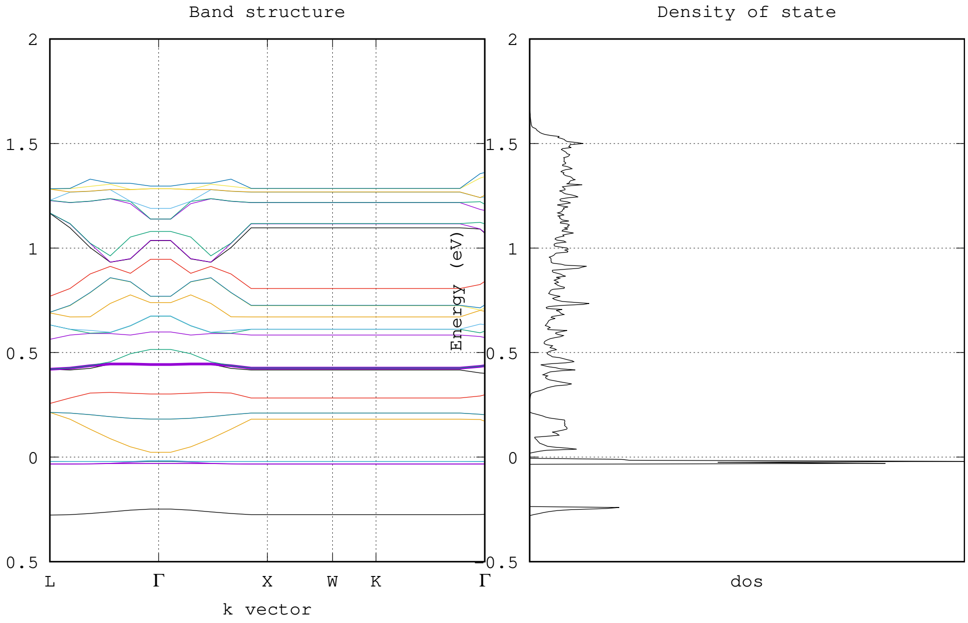


Figure 3.23: The band structure and density of state for Zinc Selenide

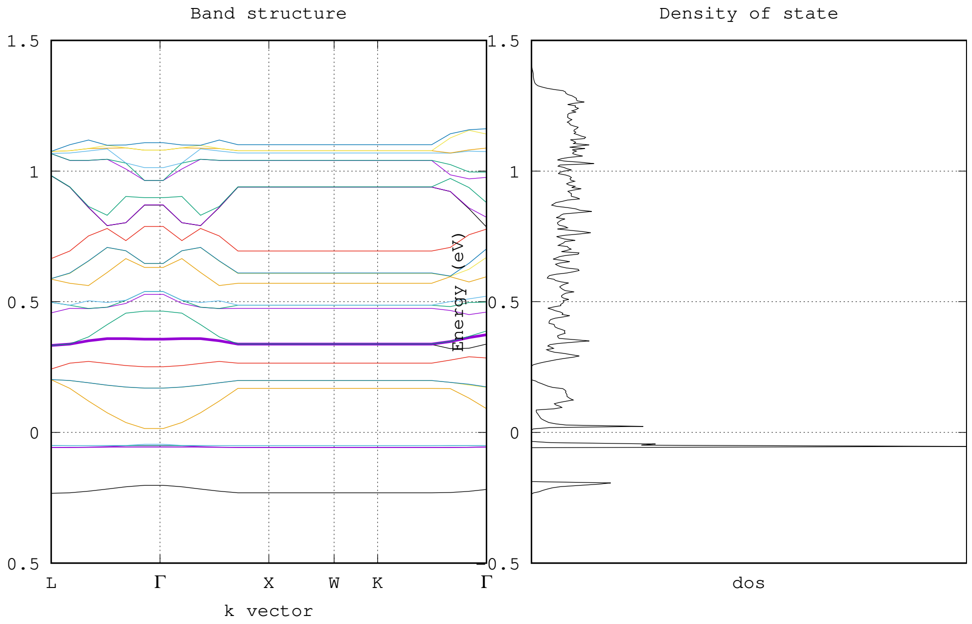


Figure 3.24: The band structure and density of state for Zinc Telluride

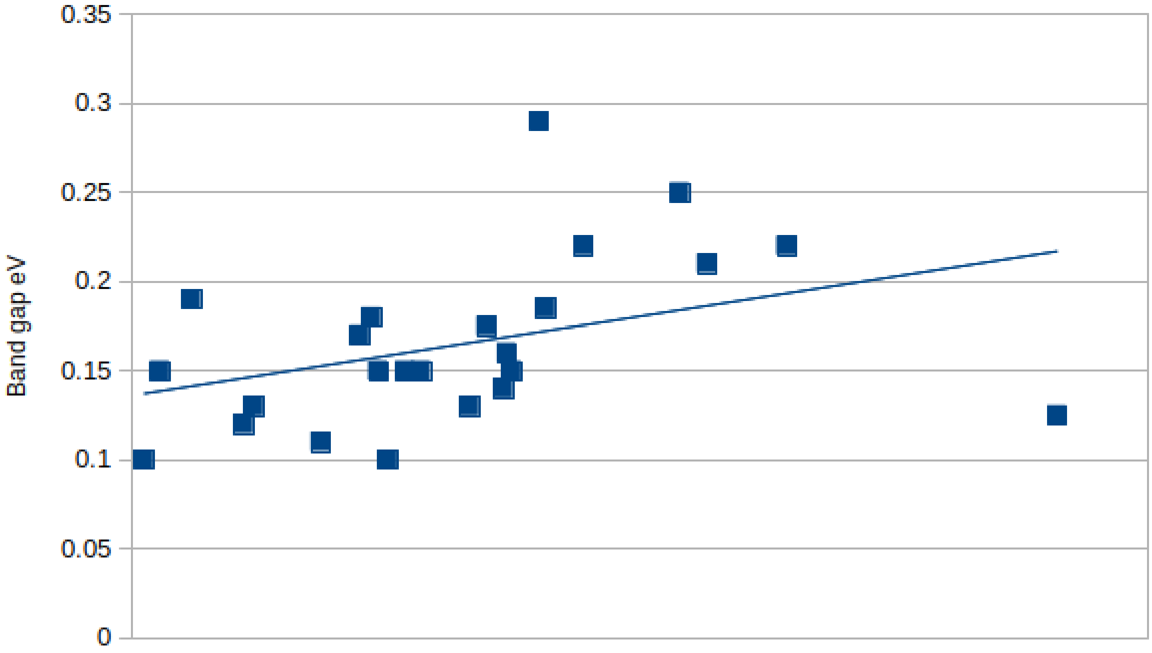


Figure 3.25: Enegy gap of various covalent solid using pbe96 functional

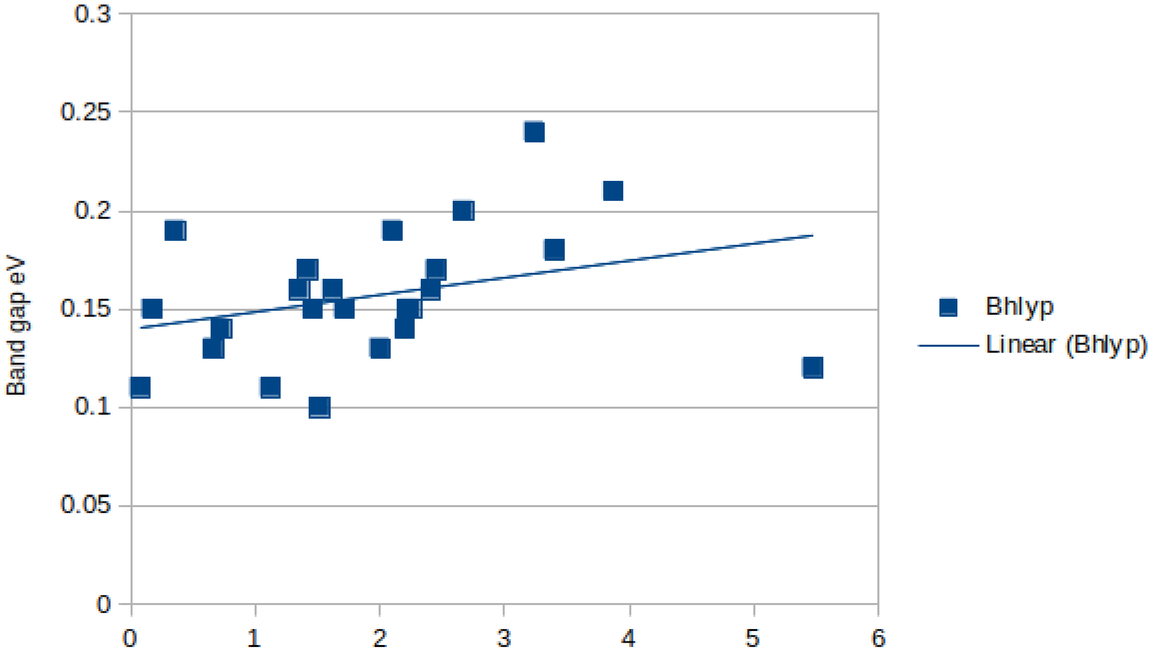


Figure 3.26: Enegy gap of various covalent solid using bhlyp functional

4

Bibliography

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